Overview of demilitarisation techniques

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1. Introduction

Demilitarization is the act of removing or neutralizing the potential of a product, in this case, an ammunition, which may, or may not, involve the destruction of its components but, requires always the destruction or the recycling of the energetic material.

Currently, the techniques used for destruction of energetic material can be considered divided into thermal or chemical. The first involve always a process of combustion or detonation, which can occur in open air or in kilns/chambers of detonation; the second involve a process such as, oxidation or biodegradation, and is under development, being unknown industrial implementations of these techniques.

Although surprising, because it seems clear that such solution carries significant environmental impacts, open burning/detonation remains a method of disposal of ammunitions used by companies in several countries of Western Europe and the USA. It is true that in the scientific community, there are people who defend that the environmental impacts associated with the processes of open air detonation are equivalent to those of the processes that include the elimination of the energetic material by combustion/detonation in a closed chamber[1]. Open burning/detonation is, undoubtedly, the cheaper elimination method and, probably, this is the main reason why it still continues to be admitted in some European countries. It should be noted that are the governments of the countries that have to incur, through their armed forces, with the increase of the cost of the prohibition of the use of this route of disposal of ammunitions. However, apart from that, either due to legislative or, with the emerging of insensitive munitions, due to technical problems this method of disposal is facing more and more obstacles. From a technical point of view, the problems are associated with the increasing difficulty in achieving the completely destruction of this type of ammunition and its energetic material, developed specifically to resist detonation by sympathy. This characteristic increases the risk of dispersion of ammunition at large distance around the place of disposal, in conditions of being used, which, in military operation fields, can provide opportunities for their illicit use. Moreover, an incomplete destruction of the energetic material has serious

[1] e.g.: An Overview of the U.S. Demil, Range, "Green" and Other Munition Management Capabilities G. Thompson, Chemical Compliance Systems, Inc., United States; AVT- Symposium on Munition and Propellant Disposal and its Impact on the Environment NATO/PFP UNCLASSIFIED+AUS AVT-177/RSY-027; Edinburgh, United Kingdom 17-20 October 2011

environmental consequences arising from the deposition of these energetic materials, partially decomposed, or not decomposed at all, in soils and groundwater.

All the other non-open detonation/open burning disposal techniques involve a sequence of operations which may be schematically described by the flow diagram shown on figure 1.

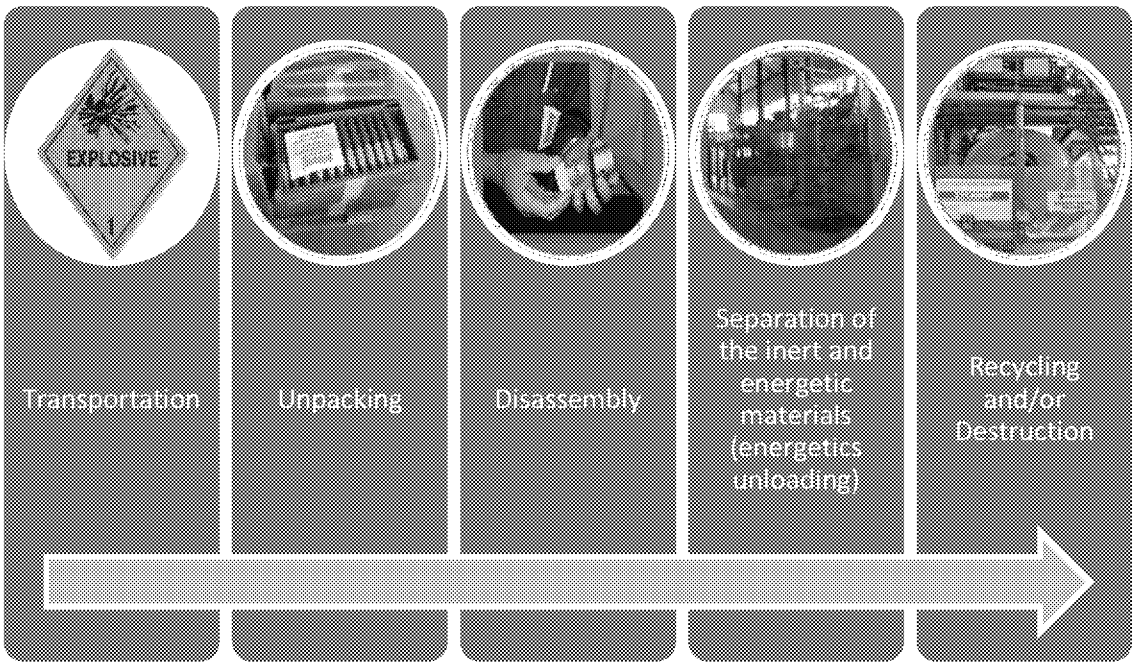

Figure 1. Flow diagram of a typical ammunition disposal process (adapted from Wilkinson and Duncan[2]).

The key process phases are the disassembly, separation or energetic unloading and the destruction and/or recycling. The double goal of the disassembly is the removal of the potential dangerous components of the ammunitions and the creation of the conditions to access to the energetic materials. The achievement of these two goals may involve the cutting or fracture of the ammunition and can be done either manually or using robotic operated equipment. Removal (or discharge) of the energetic material is the operation that normally follows: it may involve simple operations, like pouring gun propellant from cartridges, or relative complex operations of washout with steam. Finally the process ends with either the recycling of materials, done for almost all the inert materials and a part of the energetics, or their destruction.

2. Detail description of the typical ammunition disposal process

This section describes in more detail the typical steps associated with the demilitarisation process.

2.1 Disassembling and unloading or discharging

[2] Wilkinson, J., Duncan W., "Review of Demilitarization and Disposal Techniques for Munitions and Related Materials", Munitions Safety Information Analysis Center; United Nations Headquarters, Belgique January 2006

As stated before, the objective of the disassembling phase is to remove the dangerous parts of the ammunition and to provide the access to the energetic material. This later part can be achieved through simply dismounting the ammunition, however, most of the times involve cutting or fracture operations. A list of the most used disassembling techniques is shown on Table 1.

Once removed the dangerous parts of the ammunitions and obtained the access to the energetic materials follows the unloading or discharging process. Depending of the type of the energetic material, this may be done just pouring (e.g. gun propellant from most of the ammunitions cartridges) or involving melting or washout operations. A list of the most used unloading techniques is shown on table 2.

Detail descriptions of the techniques used for ammunition disassembling and discharging can be found, for example, in Wilkinson and Duncan (2006), The Best Practice Guide on the Destruction of Conventional Ammunition (2008) or in the STO TECHNICAL REPORT TR-AVT-179 - Design for Disposal of Present and Future Munitions and Application of Greener Munition Technology (2014).

Table 1. List of the most common disassembling techniques in demilitarization processes.

Disassembling	
Technique	Description
Reverse assembly	Performed at disassembling lines, using a great variety of tools, manually, by operator, or in an automatic way, involving: fuses and igniters removal; booster separation from fuses, igniters and center core igniters separated from cartridges; propellant cartridges separated from projectiles.
Mechanical downsizing	Performed manually or in automatic lines with minimum human intervention using tools that may go from a simple wrench to water or laser jet cutting machines and passing through lathe machines, saws and presses.
Cryofracture	Originally developed for chemical munitions, uses the deep temperature freezing of the ammunitions with liquid nitrogen to facilitate its fracture and the access to the energetic material.

Table 2. List of the most common discharging techniques in demilitarization processes.

Discharging (unloading)	
Technique	Description
Meltout techniques	Widely used to remove the explosives fillings from ammunition. TNT and its derivatives, such as Composition B, are easily melted poured at a temperature about 80° Celsius, and then, the molten explosives can be collected further treatment or disposal.

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High pressure water washout	Use the high pressure water washout to remove all kind of explosive filling, especially suitable for PBX removal and other non melt casted explosives.
Solvent washout	Make use of large amounts of solvents like, methylene chlorides, methyl alcohol, and acetone to dissolve the explosives. Its fundamental have a large recovery and storage facilities. This process enables the recycling of the explosives and has some environmental impacts associated with the toxicity of the solvents.

It should be noted that either the meltout either the washout based techniques can be carried out with some variations. The washout, for example, can be performed with ammonia or liquid nitrogen, while meltout can use microwave or electrical induced current to heat up and melt the energetic material. However, all of these variations are in a research or prototype development phase.

2.2 Elimination of the energetic materials

The alternatives to the destruction of the energetic materials not involving open burning or open detonation may be divided in thermal and chemical. Among the options in the first group, distinction can be made based on the type of the heat treatment and on the type of chamber or kiln use. Details of the principle of operation, installation requirements and capabilities are given on Table 3.

Table 3. List of the available techniques for the elimination of the energetic materials in demilitarization processes.

Destruction Technique	
Heat Treatment	**Chamber/Kiln**
Detonation	**Closed chamber**: Detonation of controlled amounts of energetic material or small ammunition items within a high resistance closed chamber. Fragmentation and pressure effects from the detonation are controlled by the detonation chamber. The detonation chamber may be transportable and, in many instances, incorporates a gas treatment system. It is not suitable for industrial-scale and it is specially used in the on-site destruction of explosive devices found during demining activities or the destruction of UXO (Unexploded Ordenance).
Combustion	**Close firing chamber**: This solution has been used in the demilitarization of rocket engines, as it allows the controlled ignition of a rocket motor, in a chamber, with no need for a burner or an initiation charge. The gases from the

	combustion are sent to gases treatment system so that emissions meet the legal requirements. It is a technology that involves low energy consumption and is easily transportable.
Incineration[3]	**Static or rotary kiln**: The static or rotary kiln is capable of heating the contents (ammunition, ammunition component or energetic material) up to its ignition temperature by direct or, to avoid adding additional gas to the emissions, by indirect[4] heating. The typical operating temperature is about 500°C. The material is expected to be destroyed by combustion or deflagration but, eventually, episodes of detonation may happen. It is an almost automated process, for both static and rotary kilns, capable of continuous operation, with reduced need for human resources and easily industrially. Typically, this type of furnaces works associated with more or less complex gas treatment systems.
Incineration	**Fluidized bed**: The explosive waste is injected as non detonable slurry into a bed constituted of a sand particles. These particles start to float, acting as a liquid due to the action of a hot air flow. This is a very safe concept to incinerate explosive waste, can be realized in any size.

Chemical Treatment	**Short description**
Super Critical Water Oxidation	Also known as Hydrothermal Oxidation is a suitable technique for prevent the formation of dioxins during the destruction of pyrotechnic compositions containing chlorine, irritating agents and chemical warfare agents.
Plasma Arc Pyrolysis	Consist in a reactor, equipped with a melting torch that produces a plasma arc with a temperature about 20000°C, to neutralize certain types of chemical explosives. This process needs a high amount of energy and produces a glazed composition in which the toxic compounds are captured and have to be stored in a hazardous waste storage site.
Biodegradation	Micro-organisms are used to consume ammunition related chemicals such as TNT and other explosives or propellant components. This technique is suitable for in situ remediation of contaminated military soils.

[3] Incineration should be understood in the context of this report as a combustion, detonation or any thermal degradation process within an open heated furnace, continuous operated, under controlled conditions (e.g. temperature maintained within certain limits) with off-gas treatment.
[4] For example, heating of the kiln walls using electrical resistances.

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2.3 Recycling of the energetic materials

On the contrary to what happen with the inert material (most of it metal) for which the recycling rate is over 95%, recycling of the energetic materials arising from the demilitarization processes is much scarcer. Due to the extremely restrictive demands, the (re)qualification of the demilitarized energetic material for military use would request for expensive chemical treatments that are only applicable for high value explosives like HMX. Recycling alternatives are, however, applicable to a much wider sort of demilitarized energetic materials ranging from TNT white phosphorus and passing through gun powder. A short description of three of the most used recycling options is given on Table 4. From the three alternatives the recycling for fertilization is the most complex because beyond some kind of chemical treatment for inerting it also needs qualification to be used is agriculture fertilization. On the other hand, energy recover from the energetic materials need to be done with great care due to the potential risk of an explosion and of boiler failure and prevent such risk the incineration of the energetic material within standard incineration installations need to be done with wet slurries that decrease their specific energy content. The incorporation of energetic materials from demilitarization in the production process of civil explosives arose immediately following the Second World War, but, only in the late 80s and early 90s, with the end of the Colt War, its became receiving greater attention by those responsible for the demilitarization processes. Currently, there are several companies in Europe to recycle by this way the energetic material. Problems to the implementation of this recycling route may arise from the great variability of the energetic materials to be recycling but the problem may be overcome through the use of proper homogenization techniques (creation of a single batch of energetic material from multiple small batches) and simple characterization techniques.

Table 4. Different recycling alternatives for the energetic materials from demilitarized ammunitions.

Recycling path	**Technology details**
Energy recovery	In some cases, use of the energy (heat) generated during the incineration process of the explosives and the ammunition through the installation of a recovery boiler to generate steam. Normally done within fluidized bed incinerators.
Recycling as Fertilizer	The gun powders and the explosives, mainly the nitrogen rich compositions, can be recycled in fertilizers, by processes such as hydrolysis.
Co-detonation with	Done for both TNT based explosives and propellants (rocket and gun) and

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civil explosives	involving flaking or gridding the energetic material and their mixture with slurry or emulsion explosives in percentages as high as 50% (w/w).

3. Impacts of the Demilitarization Process

The ammunitions when reach their end of life are a type of hazardous waste which need to be treated using the demilitarization techniques. The different demil techniques presents differed types of hazardous and impacts for the human health and ecosystems.

The deposition of ammunitions in a landfill, mine shafts, lakes or at sea, represent a safety hazard for very long periods of time. The dumped ammunitions sometimes can migrate from the places in which they were deposit or forgotten that the ammunition were putted their, which can lead to accidents or unintentional explosions. Moreover, the degradation of explosives is a source of toxic contamination that affects the soil, groundwater and sea water.

The thermal destructive techniques Open Burning and Open Detonation have associated to their processes the directly emission of gases (e.g. VOC, dioxins, furans, etc), particulates, and heavy metals which are a contamination source for extended areas. This emissions stays for long periods of time in the media (soil and water) being a source of contamination for the ecosystems (such as loss of biodiversity and food chain contamination) and also for human health (due to consumption of water and food contaminated with heavy metals and energetic material). Furthermore, the Open Detonation can present nuisance impacts due to vibration and noise originated from the detonation blast.

The incineration process is a controlled demilitarization technique with systems to decrease the emissions to air. However, all the explosive waste incineration processes still present some environmental impacts. The impacts related with the emissions are lower compared with the other techniques because the energy treatments need to comply with air emission regulations, so these types of facilities are equipped with chemical treatment of flue gases. These treatments have to be able to destroy volatile organic compounds (VOC), neutralize acid gases and filter out particulate and solid matter. The impacts associated to the incineration techniques are considered as indirect impacts, because they are not referent directly to the demilitarization process (such as emissions). The indirect impacts are related with the energy demand (incineration technologies involve high energy consumption) and residues. The solid waste residues (slags, scrap, fly ash, sludge) that are classified as toxic hazardous waste, due to concern about dioxins and heavy metals, is collected and disposal in other facilities. To disposal the hazardous residues from the incineration demilitarization process and neutralize them, is needed the consumption of energy and materials.

The specific industrial demilitarization processes like water washout and oxidation treatment generate large quantities of waste water contaminated with energetic material, which can be become a potential problem due to the water treatment process needed. This is one of the high concerns of the technologies in which explosives and water come into contact.

3.1 Social and economic impacts[5]

When considering the potential benefits and drawbacks of a certain demilitarization route it is important to consider the environmental constraints on the same level as the economic and social issues. The importance of these factors, however, is not the same from person to person or country to country, since it is dependent of many constrains such as strategies, politics, culture, etc. Therefore, it is difficult to achieve consensus regarding the importance given to the different factors when looking the minimization of the impacts of the process. Moreover, even when the assessment is carried out for one of the factors (e.g. environment assessment), it is difficult to select between different alternatives because they can have positive in some categories and negative in others. This problem, for the particular case of the demilitarization processes, was addressed by Alvebro *et al.* (2009) and by Duijm and Market (2002).

Alvebro *et al.* (2009) carried out a comparative life-cycle assessment of different strategies for ammunition demilitarisation (open detonation, open detonation with recycling of metals, incineration in static kiln, combination treatment of incineration with recovery of energetic material and recycling of metals). Alvebro used ten environmental categories (e.g. acidification, global warming, human toxicity, etc), and

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[5] References used in this section are:
K. Alvebro, A. Bjorklund, G. Finnveden, E. Hochschorber, J. Hagvall, A Life-Cycle Assessment of Destruction of Ammunition, J. Hazard. Mater. 2009, 170, 1101–1109.
Duijm N., Markert F., (2002), Assessment of technologies for disposing explosive waste, Journal of Hazardous Materials, pp. 137–153.
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Carlos Ferreira, José Ribeiro, Ricardo Mendes and Fausto Freire, Life-Cycle Assessment of Ammunition Demilitarization in a Static Kiln, Propellants, Explosives, Pyrotechnics Volume 38, Issue 2, pages 296–302, April 2013.
Carlos Ferreira, 2010, Avaliação de Ciclo de vida da desmilitarização de munições com valorização do material energético em explosivos civis, Master Thesis, Department of Mechanical Engineering, University of Coimbra. in Portuguese.

find difficulties to selected the best option to ammunition demilitarisation because, for all the demilitarization options in study, negative and positive impacts were found for the different environmental categories. Given so, Alvebro have decided to use weighting methods to select the preferable option. The weighting methods are an optional phase of the Life-Cycle Impact Assessment and it is need to be carried out with great caution. Moreover, it is recommended to use several weighting methods in order to achieve a more complete picture of the selected alternatives (ISO 14040, 2006). In accordance Alvebro have decided to use three weighting methods, to know:

1) Eco-indicator 99 - the weighting step is based on a panel of experts in which is given three sets of weighting factors (egalitarian perspective, hierarchism perspective, and individualist perspective) for three damage categories (Goedkoop and Spriensma, 2000);

2) EPS2000 – the weighting is based on the willingness to pay to avoid changes for five damage categories (Steen, 2000);

3) Ecotax 06 – the weighting is based on taxes and fees in Sweden for the year 2006, in which is possible to choose between two sets of weighting factors (Zhou, 2008).

Alvebro found that all the three methods gave the open detonation has presenting the worst performance, whilst the combination treatment presented the better performance for the Eco-indicator and Ecotax 06 methods. When using the EPS2000 method the incineration in static kiln and the combination treatment presented the same impacts. Alvebro could reach a conclusion with the application of weighting methods

Duijm and Market (2002) carried out a study for the environmental and safety aspects for six different techniques for ammunition demilitarization (open burning, open detonation, closed detonation, fuidised bed combustion, rotary kiln and mobile furnace). Duijm and Market (2002) considered five attributes to compare the different techniques that were assessed based on the IAEHS (Impact Assessment for Environment, Health and Safety), which objective "is to analyse the environmental impacts of noise, and emissions to air, water, and soil and to assess the risk of hazards to workers' health and safety as well as to the public". The five attributes considered were Emissions (converted to NO_2 equivalent), Waste generation (soil contamination); Area occupation; Human life (impact for culture and natural heritage); Human health (accidents).

The researched was based on two multi criteria decision analysis (MCDA) methods:

1) Reference point technique – based on raking alternative solutions with respect to the distance to the optimal solution. For each objective (five for this study) it is found the optimal and worst score. The difference for the optimal and worst score becomes

a scaling factor for each objective, in which the relative scores presents values between 0 and 1, so all alternatives can be appointed a position with the optimal solution as origin. When the objective is related to minimize impacts (or costs) the optimal score is the lower one. For this technique all the objectives have an equal weight.

2) Weighting factors from experts – based on weighting factors representing the importance which experts attributes to the different objectives. The importance that each expert subjectively assigns to the different attributes is obtained with questionnaires. The weighting factors represent the perceived importance of the different environmental and safety concerns and how they will affect the decision making. The subjective weights are multiplied with the relative scores and the results are summed, which gives a single score reflecting the importance apportioned to the different objectives defined.

When using the reference point technique, the worst performance is obtained for open burning and open detonation due to environmental impacts and to closed detonation due to safety. The other four technics presented similar performances. When using the weighting factors the technique the best performance is achieved by the fluidized bed combustion with urea injection, followed by the rotary kiln and fluidized bed combustion with bed oven. However, for this method, the differences between the different techniques are much smaller than those found for the reference point technique due to the high weight given to the safety objectives. Given so, open burning and open detonation receive quite a bit of compensation due to their intrinsic safety (involving minimum man power) which compensates their worst environmental performance.

The work of Duijm and Market (2002) also presented the conclusions for a cost-benefit analysis. The authors stated that "open burning and open detonation are very cheap techniques" whilst "Fluid Bed Combustion will cost about 150 euros and a rotary kiln between 150 and 700 euros per tonne of energetic material" (taking into account the prices for the year 2000). It was also mentioned that "mobile furnaces are expected to be more expensive than a rotary kiln" and a "closed detonation it is expected to cost more than 10 times as much and will only be competitive for minor stocks of explosive items, such as detonators, pyrotechnics and fuses" (Lauritzen, 2000).

The elaboration of this kind of studies, where beyond the environmental impacts, social and economic aspects are taken into consideration, is very important when different disposal techniques need to be alternatively considered. For the particular case of Portugal, and given the installed capacity, only alternatives to the last phase of the demilitarization process, the one responsible for the major part of the environmental impacts (Ferreira *et al.*, 2013), that now passes through the destruction of the energetic material in static kiln are being considered. The option for recycling the demilitarized energetic material for incorporation within civil explosives is known to have evident environmental benefits (Ferreira, 2010) and the social and economic impacts associated to this option, despite of the specificities of the methods used by Alvebro *et al.* (2009), may be extrapolated from the results obtained by the authors to the disposal path the combines the partial incineration of the energetic materials with off-gas treatment with partial recovery of energetic material and total recycling of metals.

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